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Guides for Short-Term Exposures of the Public to Air Pollutants

II. Guide for Hydrogen Chloride

by

The Committee on Toxicology

of the

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16. Abstracts

Upon recognition of the fact that occasional peak additions of pollutants to the ambient exposures of the public do occur, work was begun on the preparation of these guides. Primary consideration was given to literature dealing with single or intermittent brief exposures to hydrogen chloride or hydrochloric acid. The guides present threshold levels of exposure and the corresponding responses or effects on: Animals; Man; Vegetation; and Materials. The guide also presents; Short Term Public Limits (STPL's) and Public Emergency Limits (PEL's). Analytical methods for the measurement of hydrogen chloride are also included.

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Advisory Center on Toxicology
National Academy of Sciences-National Research Council

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Contract Monitor:
Dr. Vaun A. Newill, Director
Division of Health Effects Research
Air Pollution Control Office
Environmental Protection Agency
Durham, North Carolina

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INTRODUCTION

The Air Pollution Control Office of the Environmental Protection Agency has focused its initial concerns on long-term exposures of the public to air pollutants. In addition to the long-term levels there are occasional circumstances wherein the public may be exposed briefly to relatively high concentrations. For example, batch process techniques in industries may result in pulses of effluent. The testing and launching of rockets releases exhaust products. Rapidly changing meteorological conditions may result in short periods of locally high concentration of stack effluents. Accidental releases of chemicals sometimes occur in industrial areas or during transport, and may lead to exposure of the public.

Recognizing that these occasional peak additions to the ambient exposures of the public do occur, the Air Pollution Control Office has requested the assistance of the Committee on Toxicology of the National Academy of Sciences-National Research Council in providing Guides for Short-Term Exposure Limits for Air Pollutants.

In preparing these guides, the Committee utilized the criteria described in the National Academy of Sciences-National Research Council document entitled "Basis for Establishing Short-Term Inhalation Exposure Limits of the Public to Atmospheric Pollutants"(30). Primary consideration was given to literature dealing with single or intermittent brief exposures to the contaminant in question, in this case hydrogen chloride or hydrochloric acid.

Hydrogen Chloride

Hydrogen chloride (HCl) is a colorless hygroscopic gas with a molecular weight of 36.5 and a boiling point of -84.9° C. Because of its high solubility in water (82.3g/100 cc cold water), hydrogen chloride readily forms aqueous hydrochloric acid. Under normal atmospheric conditions HCl will exist as an aqueous acid aerosol; conditions of unusually low relative humidity may allow for the existence of anhydrous hydrogen chloride. The toxic effects of high concentrations of this anhydrous form may be more severe than those of the aqueous form because of the dehydrating action of the gas on exposed tissues (1).

At 25° C and 760mm Hg 1.49 mg HCl/m^3 of air is equivalent to 1 ppm.

Effects on Animals

At sufficiently high concentrations, HCl acts as a primary irritant, especially to the eyes and the moist mucous membranes of the respiratory tract. Effects of various concentrations of HCl on rabbits, cats, and guinea pigs were reported by Flury and Zernick (2) in 1931 (Table I).

Machle et al. (3) generated hydrogen chloride gas by mixing aqueous HCl with concentrated sulfuric acid and exposed rabbits, guinea pigs, and one monkey to various concentrations for various time intervals. Their observations are summarized in Table II.

Cralley (4) examined the effects of hydrogen chloride on mucociliary activity of sections of excised rabbit trachea. The hydrogen chloride was generated by mixing sodium chloride and sulfuric acid. The excised tracheal tissue was maintained in a constant temperature-humidity chamber and observed microscopically. Ciliary activity in the excised tissue ceased, without recovery, upon exposure to hydrogen chloride at 90 mg/m^3 (60 ppm) for five minutes or 45 mg/m^3 (30 ppm) for ten minutes. Concentrations of 45 mg/m^3 (30 ppm) to 600 mg/m^3 (400 ppm) for time intervals of 3.2 minutes to 0.5 minutes respectively caused reversible ciliary inhibition.

Table I

Effects of HCl Reported by Flury (2)

Species	Concentration	Time	Effects
Cats, Rabbits	100-140 ppm	up to 6 hr	Runny nose and salivation. No sequelae
Rabbits, guinea pigs	300	6 hr	Catarrh and cloudy cornea
Rabbits, guinea pigs	1350	75 min	Strong respiratory irritation and distress. Corneal opacity.
Rabbits, guinea pigs	3400	90 min	Fatalities 2-6 days post-exposure

Table II

Hydrogen Chloride Toxicity by Machle (3)

Rabbits, guinea pigs	4300 ppm	30 min	100% fatal
Rabbits, guinea pigs	700 ppm	6 hr	100% fatal
Rabbits, guinea pigs	3700 ppm	5 min	No deaths
Rabbits, guinea pigs	70 ppm	5 days,6 hr each	No effects
Rabbits, guinea pigs and one monkey	30 ppm	6 hr/day 5 days/wk 4 weeks	No effects

Effects on Man

Hydrogen chloride and hydrochloric acid act as contact irritants. Severity depends on the intensity of exposure and on the tissue involved. The epithelium and mucous membranes of the respiratory tract and the conjunctivae of the eyes are the most sensitive sites of action because the irritants are readily absorbed by these moist tissues (5, 6).

Inhalation of 1500 mg/m^3 (1000 ppm) is dangerous within one hour (1, 5). Although concentrations between 75 and 150 mg/m^3 (50 and 100 ppm) have been reported to be tolerable for periods up to one hour (1), Heyroth (7) states that normal work is impossible at concentrations in this range.

Acute Response to HCl

Depending on the severity of exposure, the physiological responses to the inhalation of irritating levels of HCl are: coughing, pain, inflammation, edema, and desquamation in the upper respiratory tract, i.e., the nasal passages and larynx. If concentrations are high enough, acute irritation may bring about constriction of the larynx and bronchi, closure of the glottis and breath holding.

Fatal inhalation of HCl would be expected only when the victim is unable to escape from the contaminated atmosphere.

Response to Repeated HCl Exposure

ten Bruggen Cate (8) has reported an increased incidence of dental erosion in workers employed in industries that use large quantities of various acids including HCl. Although he does not report the levels of acid mist in the work environment, he states that increased ventilation and other control methods reduced the incidence of erosion below that observed in poorly controlled work areas.

Bleeding of the nose and gums, and ulceration of the mucous membranes, have also been attributed to repeated occupational exposure to high levels of HCl mist (9,10).

Thresholds of Effects

Although Leonardos *et al* (11) reported the odor threshold for HCl to be 15 mg/m^3 (10 ppm), lower values have been reported by a number of others. Patty (13) states that "most people can detect 1.5-7 mg/m^3 (1-5 ppm); 7-15 mg/m^3 (5-10 ppm) is disagreeable." Elkins (14) reports all concentrations above 15 mg/m^3 (10 ppm) to be irritating, although he mentions that workers develop some apparent tolerance.

Melekhina (12), using a test panel of 16 volunteers between the ages of 17-36, reports an odor threshold for HCl of 0.39 mg/m^3 (0.26 ppm). In contrast to the method employed by Leonardos et al. (11), who considered the "odor threshold" to be the minimum concentration detectable by all the test panel members, Melekhina considered the "threshold" to be the minimum concentration detected by the most sensitive volunteer.

Effects on Vegetation

Hydrogen chloride has been reported to be of only minor concern as a phytotoxic air pollutants. Heck et al. (15), in a review of the literature, indicate that field observations of HCl injury to plants in the United States have been few.

In comparison to some of the other phytotoxic air pollutants, HCl has a relatively low order of hazard to plants. The threshold of injury for HCl is apparently 7-15 mg/m^3 (5-10 ppm) if continued for a few hours. Levels of 0.06 mg/m^3 (0.03 ppm) ozone for four hours, 0.07 mg/m^3 (0.1 ppm) hydrogen fluoride for two hours, and 0.06 mg/m^3 (0.05 ppm) ethylene for six hours are the injury thresholds for certain other phytotoxic air pollutants (18).

Viburnum and larch seedlings were killed in less than two days by exposure to HCl at 7-30 mg/m^3 (5-20 ppm). Local lesions were observed on fir, beech, and oak after exposure for one hour to 1500 mg/m^3 (1000 ppm) HCl. Exposure of maple, birch, and pear trees for 1 hr/day for 80 days to 3000 mg/m^3 (2000 ppm) produced necrosis along the leaf margins (15).

Shriner and Lacasse (in 15) exposed 28-day-old tomato plants to HCl for two hours at 7 mg/m^3 (5 ppm) and observed leaf necrosis within 72 hours of the exposure.

Damage to maple, cherry, redbud, rose, and begonia foliage, due to HCl and Cl_2 emissions from a glass-manufacturing plant, has been reported by Hindawi (16). Stack emissions from the plant averaged 490 mg/m^3 (329 ppm) HCl and 2.1 mg/m^3 (0.73 ppm) Cl_2. No air samples were taken at the site(s) of vegetation injury. High chloride levels were found in both injured and uninjured plants, so that no correlation between chloride levels and degree of injury could be made. The author concludes that chemical analysis of plant tissue is unsuitable for diagnosing chloride injury resulting from air pollution. In this regard Bohne (17) discusses some of the difficulties of determining the effects of HCl emissions on plants, e.g., (a) normal chlorine content of leaves differs greatly among species and within populations of the same species; (b) the high solubility of chlorine compounds allows for the "washout" of the chloride by precipitation or removal via the sap flow.

Guide Values for Short-Term Limits

Short-term public exposures are those occurring at predictable times and arising from single or, occasionally, repeated events. Where exposure can be predicted there is no justification for submitting the public to any appreciable risk (30).

Experimental data as well as data collected from occupational situations indicate that the chief effect of HCl upon those exposed is primary irritation, mostly of the moist mucous membranes of the upper respiratory tract.

It has been reported in the United States that the odor threshold for HCl is between 1.5 and 15 mg/m^3 (1-10 ppm), and that concentrations greater than 8-15 mg/m^3 (5-10 ppm) are disagreeable or irritating. Prevention of odor becomes a significant factor for longer exposures.

It is desirable to keep the short-term public limits below the level of irritation that may lead to singificant discomfort.

Short-Term Public Limits (STPL's)

10 min	6 mg/m^3 (4 ppm)
30 min	3 mg/m^3 (2 ppm)
60 min	3 mg/m^3 (2 ppm)
1 hr daily	3 mg/m^3 (2 ppm)
5 hr/day, 3-4 days/mo	1 mg/m^3 (0.7 ppm)

These levels are time-weighted averages not considered to present any health hazard. It should be recognized that excursions above these levels are likely to produce objectionable odors and/or irritation.

Public Emergency Limits(PEL's)

Emergency exposure limits for the public situations in which pollutants escape in an uncontrolled manner at unpredicted times and places as the result of accidents such as damage to transportation equipment or fire in a chemical storage facility. Although, under optimum conditions, the STPL's require that there be no adverse health effects, the PEL's recognize the possibility of some temporary discomfort, provided, of course, that the effect is reversible and that no serious

sequelae result from it. For this reason the following PEL's are recommended. It is felt that the impact may be no more than strong odor or, at the most, slight irritation of the mucous membranes.

10 min	10 mg/m^3 (7 ppm)
30 min	5 mg/m^3 (3 ppm)
60 min	5 mg/m^3 (3 ppm)

The preceding limits are proposed as tentative values, with the recommendation that appropriate research (perhaps such as that described in reference 22) be done in order to determine the effects of HCl inhalation on those persons having preexisting pulmonary disease. *

Effects on Materials

Although it is generally accepted that hydrochloric acid is corrosive to most metals (21), there is little information in the literature dealing with the corrosive effects of HCl at such levels as might be found in the general environment over the time periods considered in this document. Long-term effects of HCl on materials have been studied by Barton and Bartonova (19), and Hama and Curley (20).

Analytical Methods

HCl can be collected by passing contaminated air through either water or alkaline solution. While several methods are available for analysis of HCl or the chloride ion, no single method is free from interference by other contaminants that might be present in the air.

In the absence of other acids in the air, HCl levels can be determined by collecting it in a known quantity of alkali solution and titrating the excess alkali (23). However, serious errors can occur at low levels of HCl if there are also relatively high concentrations of carbon dioxide

* Most experimental studies examining the effects of HCl inhalation have been done on healthy animals and observations on humans have involved normal workers. Carefully controlled experimental work on human volunteers having preexisting pulmonary disease is necessary to determine if such persons are actually more susceptible to the effects of HCl.

in the atmosphere. By collecting the HCl in a 1:1 mixture of glycerol and water, those errors can be avoided. A small amount of silicone antifoamer will prevent foaming of the solution during sampling (24).

Elkins (25) describes two methods for the analysis of HCl in air: 1) The HCl is collected in 0.005 N NaOH, acidified with acetic acid and titrated with 0.01N $AgNO_3$, using chromate indicator (10% K_2CrO_4); 2) the HCl is collected in 0.005 N NaOH and acidified with 2 N HNO_3, (without shaking) 1 ml of 0.1 N $AgNO_3$ is added, and after 30 minutes the transmission of light through the solution is measured on a photometer - sensitivity to 1 ppm (1.5 mg/m^3) is reported for this method. Jacobs (26) describes several methods of analysis for HCl and chlorides, one of which (Volhard Method) is based on the reaction of thiocyanate with excess ferric ions to form a pink or red color that can be measured spectrophotometrically or organoleptically. A modification of this method involves the reaction of mercury thiocyanate. In this case the chloride ion releases thiocyanate, which reacts with ferric ions, forming the red complex, hexacyanatoferrate (27, 29).

A direct method for measuring chloride ions in solution utilizes a chloride ion electrode. As in the case of glass pH electrodes, the chloride ion electrode measures electrical potential across a layer of water-immiscible ion exchanger held in place by an inert porous membrane. The chloride ion electrode can be used for either individual determinations or continuous monitoring. A sensitivity down to 0.35 ppm (10-5μ) is reported (28).

The potential interference from other contaminants in any air sample may make it necessary to employ more than one method of analysis for the determination of HCl. The determination of HCl in the presence of chlorine is described in detail in reference 31.

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